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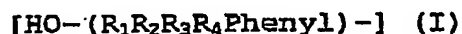
International Patent Application PCT/EP02/11258
Borealis Technology Oy et al.

New claims:

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1. A stabilized polymer composition comprising a polyolefin and an antioxidant composition for improving the long term heat stability of polyolefins, said antioxidant composition comprising:

- 10 (a) 0,01% - 0,5% by weight of at least one sterically hindered phenolic compound, wherein said phenolic compound contains at least one phenolic moiety of general formula (I):



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wherein R_1 , R_2 , R_3 or R_4 may be the same or different and at least one of R_1 , R_2 , R_3 or R_4 is selected from the group consisting of branched alkyl having 1 to 12 carbon atoms, preferably tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl, the others of R_1 , R_2 , R_3 or R_4 being H or lower alkyl having 1 to 6 carbon atoms;

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(b) 0,01% - 0,5% by weight of at least one phosphorous compound, wherein said phosphorous compound is selected from the group consisting of:

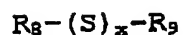
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- Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite;
- Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
- 30 - Di-stearyl-pentaerythrityl-di-phosphite; and
- Bis(2,4-dicumylphenyl)pentaerythritol diphosphite;

(c) 0,01% - 1% by weight of at least one sulphur-containing compound of general formula (III):

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(III)

wherein $x = 1$ or 2 , and wherein R_8 and R_9 may be the same or different and are selected from the group consisting of C_{10} -

5 C_{23} alkyl groups optionally being substituted with C_1 - C_{12} alkyl ester carboxylates,

wherein said % by weight values are referred to the polymer composition.

10 2. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

(a) 0,02% - 0,2% by weight of said at least one sterically hindered phenolic compound,

15 (b) 0,03% - 0,2% by weight of said at least one phosphorous compound, and

(c) 0,05% - 0,6% by weight of said at least one sulphur-containing compound of general formula (III),

20 wherein said % by weight values are referred to the polymer composition.

3. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

25 (a) 0,03% - 0,15% by weight of said at least one sterically hindered phenolic compound,

(b) 0,05% - 0,15% by weight of said at least one phosphorous compound, and

30 (c) 0,1% - 0,5% by weight of said at least one sulphur-containing compound of general formula (III),

wherein said % by weight values are referred to the polymer composition.

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4. The stabilized polymer composition of any of claims 1 to 3, wherein the phenolic compound contains at least one phenolic moiety of general formula (Ia):

5 HO-(R₁R₂R₃R₄Phenyl)-W (Ia)

wherein R₁ and R₄ being in the 2- and 6-position of the phenol residue may be the same or different and are selected from the group consisting of preferably branched C₁ to C₁₂ alkyl, particularly tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl residues, R₂ and R₃ having the meaning as given before, and W is selected from C₁ to C₁₂ alkyl, C₁ to C₁₂ alkoxy, C₁ to C₁₂ alkyl carboxylate or C₁ to C₁₂ alkyl substituted by another group of the formula HO-(R₁R₂R₃R₄Phenyl)-, wherein R₁ to R₄ have the meaning as indicated before.

5. The stabilized polymer composition of any of claims 1 to 4, wherein the sulphur-containing compound of general formula (III):



is selected from Di(C₁-C₂₀)alkyl-(S)_x-di-carboxylate wherein the carboxylic acid is selected from C₁ to C₁₂ alkyl carboxylic acids.

6. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:

- 2,6-Di-tert.-butyl-4-methyl phenol;
- Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;

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- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
- 2,2'-Thiodiethylene-bis-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- 5 - Calcium-(3,5-di-tert.-butyl-4-hydroxy benzyl monoethyl-phosphonate);
- 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-isocyanurate;
- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl) butanoic
- 10 acid)-glycolester;
- 4,4'-Thiobis (2-tert.-butyl-5-methylphenol);
- 2,2'-Methylene-bis(6-(1-methyl-cyclohexyl)para-cresol);
- N,N'-hexamethylene bis(3,5-di-tert. Butyl-4-hydroxy-hydrocinnamamide;
- 15 - 2,5,7,8-Tetramethyl-2(4',8',12'-trimethyltridecyl)chroman-6-ol;
- 2,2'-Ethylidenebis(4,6-di-tert.-butylphenol);
- 1,1,3-Tris(2-methyl-4-hydroxy-5-tert.-butylphenyl)butane;
- 20 - 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;
- 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane;
- 25 - 1,6-Hexanediyl-bis(3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene-propanoate);
- 2,6-Di-tert.-butyl-4-nonylphenol;
- 3,5-Di-tert.-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris (2-hydroxyethyl)-s-triazine-2,4,6(1H,3H,5H)-
- 30 trione;
- 4,4'-Butylidenebis(6-tert. Butyl-3-methylphenol);
- 2,2'-Methylene bis (4-methyl-6-tert.-butylphenol);
- 2,2-Bis(4-(2-(3,5-di-t-butyl-4-hydroxyhydrocinnamoyloxy))ethoxyphenyl))propane;

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- Triethyleneglycol-bis-(3-tert.-butyl-4-hydroxy-5 methylphenyl) propionate;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-

hydroxy-, C₁₃-C₁₅-branched and linear alkyl esters;

- 5 - 6,6'-Di-tert.-butyl-2,2'-thiodi-p-cresol;
- Diethyl((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl) phosphonate;
- 4,6-Bis(octylthiomethyl)o-cresol;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)4-
- 10 hydroxy-, C₇-C₉-branched and linear alkyl esters;
- 1,1,3-Tris[2-methyl-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-5-t-butylphenyl] butane; and
- Butylated reaction product of p-cresol and dicyclopentadiene.

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7. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is selected from the group consisting of:

- Di-stearyl-thio-di-propionate;
- 20 - Di-palmityl/thio-di-propionate;
- Di-lauryl-thio-di-propionate;
- Di-tridecyl-thio-di-propionate;
- Di-myristyl-thio-di-propionate;
- Pentaerythritol octyl thiodipropionate;
- 25 - Lauryl-stearyl-thio-di-propionate;
- Di-octadecyl-disulphide;
- Di-tert-dodecyl-disulphide and
- Pentaerythritol-tetrakis-(3-laurylthiopropionate)

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8. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:

- Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;

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- Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;
- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
- 5 - 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-isocyanurate;
- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl)butanoic acid)-glycolester; and
- 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro
10 (5,5)undecane.

9. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is
15 Di-stearyl-thio-di-propionate or Di-tert-dodecyl-disulphide.

10. The stabilized polymer composition of any of any of the preceding claims, wherein

- (a) the sterically hindered phenolic compound is 1,3,5-
20 Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione or pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;

(b) the phosphite compound is bis(2,4-dicumylphenyl) pentaerythritol diphosphite; and

- 25 (c) the sulphur-containing compound is Di-stearyl-thio-di-propionate.

11. The stabilized polymer composition of any of claims 1-10, wherein said composition further comprises metal.
30 deactivators and/or UV-stabilisers.

12. The stabilized polymer composition of claim 11, wherein said UV-stabilizers are sterically hindered amines.

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13. The stabilized polymer composition of any of the preceding claims, wherein said polyolefin is a homo- or co-polymer of polyethylene, polypropylene and polybutadiene.

5 14. Use of the antioxidant composition as defined in any of claims 1-11 for reducing degradation of a polyolefin material during processing and end use of said polyolefin material.

10 15. The use of claim 14 for increasing long term thermal stability of the polyolefin material.

15 16. Method for producing a polyolefin article having an improved long term thermal stability against ageing by radical degradation processes comprising the steps of:
 (a) providing an unstabilised base polyolefin material;
 (b) adding to said base polyolefin material the antioxidant composition as defined in any of the preceding claims;
20 (c) converting the composition obtained in step (b) in a melt-forming process; and
 (d) confectioning the polyolefin material obtained in step (c).

25 17. The method of claim 16 further comprising adding other stabilisers and/or modifiers before the converting step c).

30 18. The method of any of claims 16 or 17, wherein the converting step includes injection moulding, blow moulding, rotational moulding and extrusion.

35 19. The method of any of claims 16 to 18, wherein the confectioning step includes cutting, lamination and/or welding:

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20. Polyolefin article having an increased long term ageing stability obtained by the method of any of claims 20-

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